

Rotational line strengths for the CN $B^2\Sigma^+ - X^2\Sigma^+$ (5,4) band

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Rotational line strengths, computed from eigenvectors of Hund's case (a) matrix representations of the upper and lower Hamiltonians using Wigner-Witmer basis functions, show a larger than expected influence from the well known perturbation in the (5,4) band. Comparisons with National Solar Observatory experimental Fourier transform spectroscopy data reveal nice agreement of measured and predicted spectra.

Keywords: Diatomic spectroscopy, rotational line strengths, Hönl-London factors, cyanide spectra violet band perturbations

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INTRODUCTION

The CN violet $B^2\Sigma^+ - X^2\Sigma^+$ band system is one of the most studied band systems. Ram *et al.* [1] and Brooke *et al.* [2] have summarized the available experimental and theoretical information. Of the many known bands in the violet system, only the (5,4) band is considered here. This band exhibits a weak, quantitatively understood perturbation [4] caused by mixing of the $v = 17$ level of $A^2\Pi$ with the $v = 5$ level of $B^2\Sigma^+$. The particular perturbation of the CN (5,4) band is evaluated in this work by isolating the spectral features of this band that is part of the CN violet system. Numerical diagonalizations of upper and lower Hamiltonians with and without the perturbation are investigated and compared with available experimental spectra. The simulations rely on determining rotational strengths without parity-partitioned Hamiltonians. It is anticipated that the investigated (5,4) band modifications can be possibly confirmed with the new PGOPHER program recently released by Western [3].

CN (5,4) BAND SPECTRA

For the computation of rotational spectra, the square of transition moments are numerically computed using the eigenvectors of upper and lower Hamiltonians. This approach can also be selected in the new PGOPHER program [3]. For the diatomic molecule, the results effectively yield the Hönl-London factors yet we do not utilize tabulated Hönl-London factors that are available in standard textbooks. Table I and Figures 1 and 2 compare results obtained with and without taking into account the mixing. Results of modeling the angular momentum states of the upper $v = 5$ vibrational level as a mixture of $^2\Sigma$ and $^2\Pi$ Hund's case (a) basis functions, a so-called “de-perturbation” or perturbation analysis, agree well that of Ito *et al.* [4] whose used the line position measurements of Engleman [5]. The 100 lines of the more recent data of Ram *et al.* [1] were fitted with a standard deviation of 0.025 cm^{-1} . Failure to include spin-orbit mixing of the $B^2\Sigma^+$ and $A^2\Pi$ basis states increased the standard deviation to 0.25 cm^{-1} .

TABLE I. Lines in the CN $B^2\Sigma^+ - X^2\Sigma^+$ (5,4) band near the perturbation. $\tilde{\nu}$ are the fitted line positions, $S(J', J)$ are the rotational line strengths computed in the fitting algorithm. $S^{(0)}(J', J)$ and $\Delta\tilde{\nu}^{(0)}$ are the line strengths and errors in the fitted line positions, respectively, when the off-diagonal spin-orbit coupling constants $\langle AL+ \rangle$ and $\langle BL+ \rangle$ are set equal to 0. Spin-orbit mixing of $B^2\Sigma^+$ and $A^2\Pi$ shifts the upper e parity levels. An error in the $\tilde{\nu}(J', J)$ associated with these upper e parity levels is produced if the mixing is ignored. A relatively large fractional error [*e.g.*, $-3.974/17.455$ versus $-1.870/28032$ for $R_{11}(12.5)$] can occur in the rotational line strengths, $S(J', J)$.

J'	J	p'	$\tilde{\nu}$	$S_{J',J}$	$\Delta\tilde{\nu}$	$S_{J',J}^{(0)}$	$\Delta\tilde{\nu}^{(0)}$
9.5	8.5	$R_{11} -e$	28013.117	9.474	-0.010	9.474	0.337
9.5	8.5	$R_{22} +f$	28017.421	9.474	0.001	9.474	-0.059
10.5	9.5	$R_{11} +e$	28016.992	9.1988	-0.004	10.476	0.600
10.5	9.5	$R_{22} -f$	28021.651	11.171	-0.000	10.476	-0.067
11.5	10.5	$R_{11} -e$	28020.540	7.868	-0.041	11.478	1.193
11.5	10.5	$R_{22} +f$	28025.866	12.240	0.006	11.478	-0.067
12.5	11.5	$R_{22} -f$	28030.125	13.288	0.007	12.480	-0.072
12.5	11.5	$R_{11} +e$	28030.431	13.812		12.480	
13.5	12.5	$R_{11} -e$	28032.081	17.455	-0.053	13.481	-1.870
13.5	12.5	$R_{22} +f$	28034.428	14.325	0.011	13.481	-0.073
14.5	13.5	$R_{11} +e$	28035.672	17.919	-0.005	14.483	-1.102
14.5	13.5	$R_{22} -f$	28038.773	15.356	0.013	14.483	-0.076
15.5	14.5	$R_{11} -e$	28039.742	18.442	0.007	15.484	-0.807
15.5	14.5	$R_{22} +f$	28043.161	16.383	0.009	15.484	-0.084
16.5	15.5	$R_{11} +e$	28043.989	19.132	0.011	16.485	-0.655
16.5	15.5	$R_{22} -f$	28047.590	17.405	0.006	16.485	-0.091

The table and synthetic spectra reveal that the changes caused by spin-orbit mixing are relatively very much larger for the rotational line strengths, $S(J', J)$, than for the line positions, $\tilde{\nu}$. The simulation results compare nicely with measured spectra [1] available from the National Solar Observatory (NSO) at Kitt Peak [6]. Figure 3 displays the recorded and simulated spectra for a resolution of 0.03 cm^{-1} .

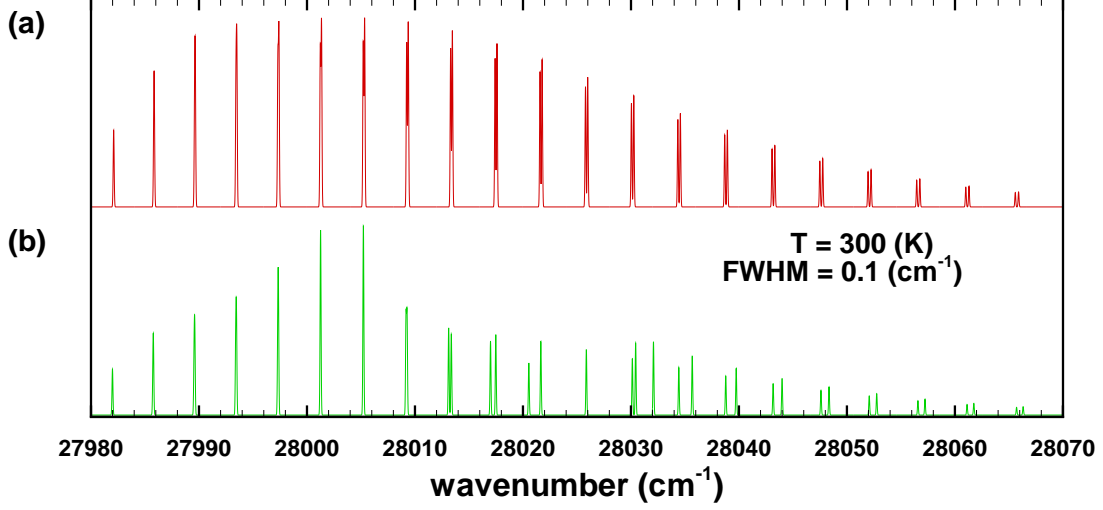


FIG. 1. Synthetic emission spectra showing the influence of inclusion of the $v = 17, A^2\Pi$ basis in the upper $v = 5$ state of the CN violet (5,4) band. In the upper spectrum, (a), the upper states are pure $^2\Sigma^+$. The $v = 17, A^2\Pi$ energy eigenvalues lie very near the $v = 5, B^2\Sigma^+$ eigenvalues, and this explains the large influence of the $A^2\Pi$ basis. In the lower spectrum, (b), the upper states are treated as the sum $c_\Sigma ^2\Sigma^+ + c_\Pi ^2\Pi$ with $c_\Sigma \gg c_\Pi$. Only R branch lines are shown here, including those given in Table I.

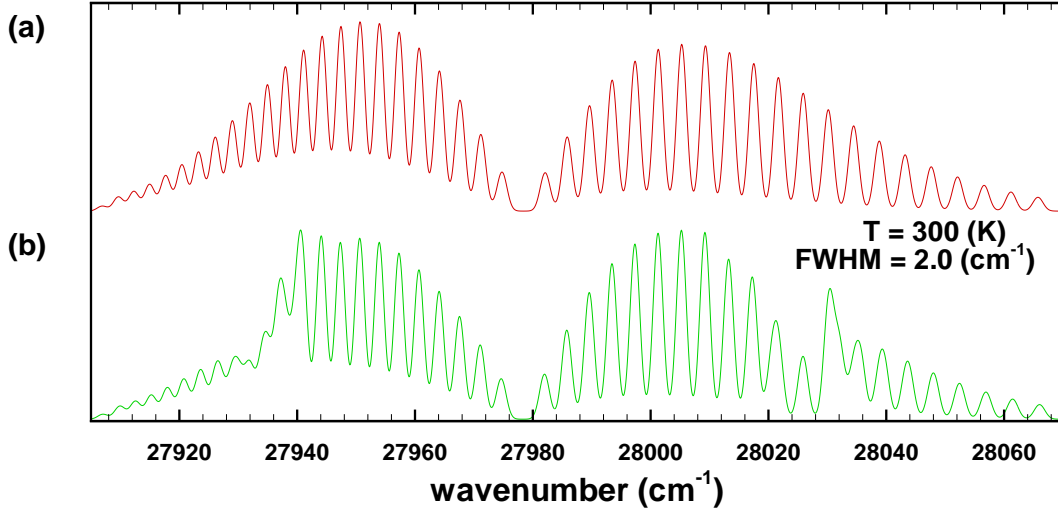


FIG. 2. The lower resolution spectra include both the P and R branches. (a) pure, (b) addition of a small amount of $^2\Pi$ to the upper basis affects the lower spectrum of the violet (5,4) band even at low resolution.

The influence of $^2\Sigma^+ + ^2\Pi$ mixing on the rotational line strengths, $S(J', J)$, was recognized because computation of $S(J', J)$ is an integral part of the unique line position fitting algorithm. Upper and lower Hamiltonian matrices in the Hund's case (a) basis are numerically diagonalized, and the spectral line vacuum wavenumber $\tilde{\nu}$ is the difference between upper and lower Hamiltonian eigenvalues. To determine which of the many eigenvalue differences represent allowed spectral lines, the factor $S(J', J)$ is computed from the upper and lower eigenvectors for each eigenvalue difference. A non-vanishing $S(J', J)$ denotes an allowed diatomic spectral line. Parity partitioned effective Hamiltonians are not used. Parity and branch designation are not required in the fitting algorithm. Input data to the fitting

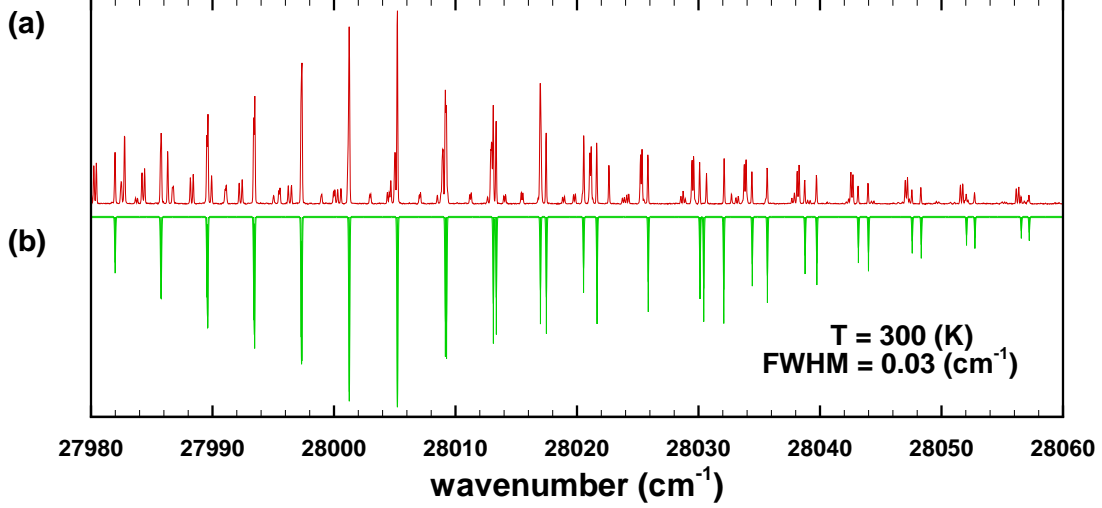


FIG. 3. Comparison of measured and simulated spectra. (a) Segment of the recorded [1] Fourier transform spectrum 920212R0.005 [6], (b) computed spectrum for a temperature of 300 K and a spectral resolution of 0.03 cm^{-1} . The computed (5.4) band is flipped vertically to show how the predicted line positions of the R-branch match the vacuum wavenumbers of the experimental spectrum.

program is a table of vacuum wavenumber $\tilde{\nu}$ versus J' and J . The non-vanishing of the rotational strength is the only selection rule used. Applications of this rule leads to the establishment of spectral data bases for diatomic molecular spectroscopy of selected transitions [7]. Over and above the PGOPHER program [3], there are other extensive efforts in predicting diatomic molecular spectra including for instance the so-called DUO program [8] for diatomic spectroscopy.

WIGNER-WITMER DIATOMIC EIGENFUNCTION

The Hund's case (a) basis functions were derived from the Wigner and Witmer [9] diatomic eigenfunction,

$$\langle \rho, \zeta, \chi, \mathbf{r}_2, \dots, \mathbf{r}_N, r, \theta, \phi | nvJM \rangle = \sum_{\Omega=-J}^J \langle \rho, \zeta, \mathbf{r}'_2, \dots, \mathbf{r}'_N, r | nv \rangle D_{M\Omega}^{J*}(\phi, \theta, \chi). \quad (1)$$

The coordinates are ρ the distance of one electron (the electron arbitrarily labeled 1 but it could be any one of the electrons) from the internuclear vector $\mathbf{r}(r, \theta, \phi)$, the distance ζ of that electron above or below the plane perpendicular to \mathbf{r} and passing through the center of mass of the two nuclei (the coordinate origin), the angle χ for rotation of that electron about the internuclear vector \mathbf{r} , and the remaining electronic coordinates $\mathbf{r}_2, \dots, \mathbf{r}_N$ in the fixed and $\mathbf{r}'_2, \dots, \mathbf{r}'_N$ in the rotating coordinate system. The vibrational quantum number v has been extracted from the quantum numbers collection n which represents all required quantum numbers except J , M , Ω , and v . The Wigner-Witmer diatomic eigenfunction has no application in polyatomic theory, but for the diatomic molecule the exact separation of the Euler angles is a clear advantage over the Born-Oppenheimer approximation for the diatomic molecule in which the angle of electronic rotation, χ , is unnecessarily separated from the angles describing nuclear rotation, θ and ϕ . Equation (1) can be derived by writing the general equation for coordinate (passive) rotations α , β , and γ of the eigenfunction, replacing two generic coordinate vectors with the diatomic vectors $\mathbf{r}(r, \theta, \phi)$ and $\mathbf{r}'(\rho, \zeta, \chi)$, and equating the angles of coordinate rotation to the angles of physical rotation ϕ , θ , and ϕ . The general equation for coordinate rotation holds in isotropic space, and therefore the quantum numbers J , M , and Ω in the Wigner-Witmer eigenfunction include all electronic and nuclear spins. If nuclear spin were to be included, J , M , and Ω would be replaced by F , M_F , and Ω_F , but hyperfine structure is not resolved in the (5, 4) band data reported by [1], and Eq. (1) is written with the appropriate spectroscopic quantum numbers.

It is worth noting that the rotation matrix element $D_{M\Omega}^J(\phi, \theta, \chi)$ and its complex conjugate $D_{M\Omega}^{J*}(\phi, \theta, \chi)$ do not fully possess the mathematical properties of quantum mechanical angular momentum. It is well known that a sum of Wigner D -functions is required to build an angular momentum state. The equation

$$J'_\pm D_{M\Omega}^{J*}(\phi, \theta, \chi) = \sqrt{J(J+1) - \Omega(\Omega \mp 1)} D_{M, \Omega \mp 1}^{J*}(\phi, \theta, \chi) \quad (2)$$

is not a phase convention [10] [11] [12] but a mathematical result readily obtained from Eq. (1) and

$$J'_\pm |J\Omega\rangle = \sqrt{J(J+1) - \Omega(\Omega \pm 1)} |J, \Omega \pm 1\rangle, \quad (3)$$

in which the prime on the operator J'_\pm indicates that it is written in the rotated coordinate system where the appropriate magnetic quantum number Ω .

HUND'S BASIS FUNCTIONS

The Hund's case (a) basis function based upon the Wigner-Witmer diatomic eigenfunction is

$$|a\rangle = \langle \rho, \zeta, \chi, \mathbf{r}'_2, \dots, \mathbf{r}'_N, r, \theta, \phi | nvJM\Sigma\Lambda\Sigma\Omega \rangle = \sqrt{\frac{2J+1}{8\pi^2}} \langle \rho, \zeta, \mathbf{r}'_2, \dots, \mathbf{r}'_N, r | nv \rangle |S\Sigma\rangle D_{M\Omega}^{J*}(\phi, \theta, \chi). \quad (4)$$

As noted above, a sum of $|a\rangle$ basis functions is required to build an eigenstate of angular momentum. The basis function would also not be an eigenstate of the parity operator. The case (a) matrix elements, $p_{ij}^{(a)}$, of the parity operator \mathcal{P} ,

$$p_{ij}^{(a)} = p_\Sigma(-)^J \delta(J_i J_j) \delta(\Omega_i, -\Omega_j) \delta(\Lambda_i, -\Lambda_j) \delta(n_i n_j), \quad (5)$$

show that a single $|a\rangle$ basis function is not an eigenstate of parity. The procedure called parity symmetrization adds $|JM\Omega\rangle$ and $|JM, -\Omega\rangle$ basis functions thereby destroying the second magnetic quantum number Ω and yielding a function which at least possesses the minimal mathematical properties of an eigenstate of angular momentum, parity, and the other members of the complete set of commuting operators. The general procedure would be to continue adding basis functions to the upper and lower bases until eigenvalue differences between the upper and lower Hamiltonians accurately predict measured line positions.

THE UPPER HAMILTONIAN MATRIX FOR THE (5,4) BAND

Electronic spin \mathbf{S} interactions with electronic orbital momentum \mathbf{L} and nuclear orbital momentum \mathbf{R} produce both diagonal and off-diagonal matrix elements in the Hund's case (a) representation of the Hamiltonian. The off-diagonal elements connect different basis states. For example, both of the mentioned spin orbit interactions connect $^2\Sigma^+$ and $^2\Pi$. Because van Vleck transformed Hamiltonians are not used, the appropriate parameters for the strength of these interactions are $\langle AL+ \rangle$ and $\langle BL+ \rangle$. Table II lists the molecular parameters used in the Hamiltonian matrices. Tables III and IV show the Hamiltonian matrices without and with spin-orbit interactions, respectively.

A DIATOMIC LINE POSITION FITTING ALGORITHM

A basic tool for the diatomic spectroscopist is a computer program that accepts a table of experimentally measured vacuum wave numbers $\tilde{\nu}_{\text{exp}}$ versus J' and J , and outputs a set of molecular parameters with which one can reproduce the $\tilde{\nu}_{\text{exp}}$ with a standard deviation comparable to the estimated experimental error. In practice, an experimental line list frequently shows gaps, *viz.* spectral lines are missing. Following a successful fitting process, one can use the molecular parameters to predict all lines. A computed line list is especially useful when it includes the Condon and Shortley [14] line strength from which the Einstein coefficients and oscillator strength [15] [16] and the HITRAN line strength [17] can be calculated. A feature of the line fitting program described below is its use of non-zero rotational strengths (see Eq. (8) below) to mark which of the many computed differences between upper and lower term values represents the vacuum wavenumber of an allowed spectral line. Consequently, the fitting process creates a complete line list including rotational factors. Parity plays no part in the fitting process, but the same orthogonal matrix that

	$X^2\Sigma^+$	$B^2\Sigma^+$	$A^2\Pi$
	$v = 4$	$v = 5$	$v = 17$
B_v	1.820866(13)	1.845727(13)	1.404833
D_v	$6.172(36) \times 10^{-6}$	$8.003(38) \times 10^{-6}$	5.66×10^{-6}
A_v			-50.5253
γ_v	$-1.98(43) \times 10^{-4}$	$-1.921(44) \times 10^{-2}$	
γ_{D_v}	$-1.98(43) \times 10^{-4}$		
T_v	8011.7871	35990.1780(25)	36010.5732
$<AL+>$		4.25(0.03)	
$<BL+>$		0.0205(0.001)	

TABLE II. Molecular parameters used in this work that relies on Hamiltonians that are not parity-partitioned. Values not followed by a number in parenthesis were held fixed or an error estimate was not computed. A value in parenthesis is the standard deviation in the fitted value. Parameters for the $A^2\Pi$ state were fitted by the Nelder-Mead minimization algorithm using values given by Brooke *et al.* [2] as trial values. Error estimates were not computed, and the values of Brooke *et al.* [2] were only very slightly changed.

	v			5	5	17	17	17	17
	Λ			0	0	-1	-1	1	1
	Σ			-0.5	0.5	-0.5	0.5	-0.5	0.5
v	Λ	Σ	Ω	-0.5	0.5	-1.5	-0.5	0.5	1.5
5	0	-0.5	-0.5	36351.6409	-25.6707	0	0	0	0
5	0	0.5	0.5	-25.6707	36351.6409	0	0	0	0
17	-1	-0.5	-1.5	0	0	36257.6340	-19.5866	0	0
17	-1	0.5	-0.5	0	0	-19.5866	36310.9646	0	0
17	1	-0.5	0.5	0	0	0	0	36310.9646	-19.5866
17	1	0.5	1.5	0	0	0	0	-19.5866	36257.6340
E_{nvJ}				36377.3116	36325.9702	36251.2135	36317.3851	36317.3851	36251.2135

TABLE III. Hamiltonian matrix for states modeled as the mixture of $^2\Sigma^+$ and $^2\Pi$ basis states. Off-diagonal spin-orbit coupling has been removed. Consequently, the 2×2 matrices along the main diagonal are independent, and could be individually diagonalized. The bottom row contains the energy eigenvalues. Using matrices like these to model upper states of the CN violet (5,4) band, the 100 experimental spectral lines reported by Ram *et al.* [1] were fitted with a standard deviation of 0.25 cm^{-1} . This Hamiltonian was computed for $\langle AL+ \rangle = \langle BL+ \rangle = 0$ but is otherwise identical to the Hamiltonian in Table IV. Standard Hund's case (a) matrix elements [10] [12] were used.

				v	5	5	17	17	17	17
				Λ	0	0	-1	-1	1	1
				Σ	-0.5	0.5	-0.5	0.5	-0.5	0.5
v	Λ	Σ	Ω		-0.5	0.5	-1.5	-0.5	0.5	1.5
5	0	-0.5	-0.5	36351.6409	-25.6707		2.8566	2.3274	2.8639	0
5	0	0.5	0.5	-25.6707	36351.6409		0	2.8639	2.3274	2.8566
17	-1	-0.5	-1.5	2.8566	0	36257.6340	-19.5866		0	0
17	-1	0.5	-0.5	2.3274	2.8639	-19.5866	36310.9646		0	0
17	1	-0.5	0.5	2.8639	2.3274	0	0	36310.9646	-19.5866	
17	1	0.5	1.5	0	2.8566	0	0	-19.5866	36257.6340	
E_{nvJ}				36377.3957	36327.7869	36250.9625	36317.3525	36315.8194	36251.1620	

TABLE IV. Off-diagonal spin-orbit coupling 6×6 matrix. From the three independent 2×2 matrices of Table III, the off-diagonal matrix elements mix the Hund's case (a) basis states, and the standard deviation of the spectral line fit mentioned in Table III is reduced by a factor of 10 to 0.025 cm^{-1} . The spin-orbit coupling constants $\langle AL+ \rangle = 4.25(0.03)$ and $\langle BL+ \rangle = 0.205(0.001)$ were used in computation of this Hamiltonian. This single 6×6 matrix describing $^2\Pi - ^2\Sigma^+$ mixing can be compared with the two 3×3 parity partitioned matrices of Brown and Carrington [13].

diagonalizes the case (a) Hamiltonian matrix will also diagonalize the case (a) parity matrix whose elements are given in Equation (5). The $p = \pm 1$ parity eigenvalue becomes a computed quantity, and the e/f parity designation is established from the parity eigenvalue using the accepted convention Brown *et al.* [18].

Trial values of upper and lower state molecular parameters, typically taken from previous works by other for the band system in question, are used to compute upper H' and lower H Hamiltonian matrices in the case (a) basis given by Eq. (4) for specific values of J' and J . The upper and lower Hamiltonians are numerically diagonalized,

$$T' = \tilde{U}' H' U' \quad (6a)$$

$$T = \tilde{U} H U \quad (6b)$$

giving the upper T' and lower T term values. The vacuum wavenumber $\tilde{\nu}$ is determined,

$$\tilde{\nu}_{ij} = T'_i - T_j, \quad (7)$$

and the rotational strength is evaluated,

$$S_{ij}(J', J) = (2J + 1) \left| \sum_n \sum_m \tilde{U}'_{in} \langle J\Omega; q, \Omega' - \Omega | J'\Omega' \rangle U_{mj} \delta(\Sigma'_n \Sigma_m) \right|^2. \quad (8)$$

The degree of the tensor operator, q , responsible for the transitions amounts to $q = 1$ for electric dipole transitions. For a non-zero rotational factors, $S(J', J)$, the vacuum wavenumber $\tilde{\nu}_{ij}$ is added to a table of computed line positions to be compared with the experimental list $\tilde{\nu}_{\text{exp}}$ versus J' and J . The Clebsch-Gordan coefficient, $\langle J\Omega; q, \Omega' - \Omega | J'\Omega' \rangle$, is the same one appearing in the pure case (a) - case (a) formulae for $S(J', J)$. For a specific values of J' and J , one constructs tables for $\tilde{\nu}_{\text{exp}}$ and computed $\tilde{\nu}_{ij}$. The errors $\Delta\tilde{\nu}_{ij}$,

$$\Delta\tilde{\nu}_{ij} = \tilde{\nu}_{ij} - \tilde{\nu}_{\text{exp}}, \quad (9)$$

are computed where each $\tilde{\nu}_{ij}$ is the one that most closely equals one of the $\tilde{\nu}_{\text{exp}}$. Once values of $\tilde{\nu}_{ij}$ and $\tilde{\nu}_{\text{exp}}$ are matched, each is marked unavailable until a new list of $\tilde{\nu}_{ij}$ is computed. The indicated computations are performed for all values of J' and J in the experimental line list, and corrections to the trial values of the molecular parameters are subsequently determined from the resulting $\Delta\tilde{\nu}_{ij}$. The entire process is iterated until the parameter corrections become negligibly small. As this fitting process successfully concludes, one obtains a set of molecular parameters that predict the measured line positions $\tilde{\nu}_{\text{exp}}$ with a standard deviations that essentially equal the experimental estimates for the accuracy of the $\tilde{\nu}_{\text{exp}}$.

DISCUSSION

The influence on intensities in the (5,4) band of the CN violet system caused by the weak spin-orbit mixing, Figs. 1 and 2, is significantly larger than initially anticipated. This was noticed because computation of the rotational strengths is an integral part of our line position fitting program. The eigenvectors that diagonalize the Hamiltonian to yield fitted line position $\tilde{\nu}$ also yield $S(J', J)$. In established diatomic molecular practice, Hönl-London factors are determined independently of line positions. Analytical approximations utilize the parameter $Y = A/B$ to account for the influence of spin-orbit interaction on $S(J', J)$. Kovács [19] gives many examples, Li *et al.* [20] give a more recent application. These analytical approximations can accurately account for intermediate spin-orbit coupling which smooth transitions between case (a) and case (b) with increasing J' and J , but show limited sensitivity to abrupt changes in $S(J', J)$ near perturbations such as those seen the (5, 4) band in the CN violet system.

CONCLUSION

The Wigner-Witmer diatomic eigenfunction makes it possible to form an exact, mathematical connection between computation of $\tilde{\nu}$ and $S(J', J)$ in a single algorithm. The concept of the non-vanishing rotational strengths as the omnipotent selection rule initially conceived as a simplifying convenience in a computer algorithm is now seen to be more valuable, as evidenced in this work's analysis of the CN (5,4) band perturbations by isolating a specific branch. Future work is planned for comparisons of the CN (10,10) band spectra that include perturbation and that show promising agreements with experiments and PGOPHER predictions.

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REFERENCES

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- [1] Ram RS, Davis SP, Wallace L, Englman R, Appadoo DRT, Bernath PF. Fourier transform emission spectroscopy of the $B^2\Sigma^+ - X^2\Sigma^+$ system of CN, J Mol Spectrosc 2006; 237:225-231.
 - [2] Brooke JSA, Ram RS, Western CM, Li G, Schwenke DW, Bernath PF. Einstein A Coefficients and Oscillator Strengths for the $A^2\Pi - X^2\Sigma^+$ (Red) and $B^2\Sigma^+ - X^2\Sigma^+$ (Violet) Systems and Rovibrational Transitions in the $X^2\Sigma^+$ State of CN. ApJS 2014; 210:23.
 - [3] Western CM. PGOPHER: A program for simulating rotational, vibrational and electronic spectra. J Quant Spectrosc Rad Transfer 2017; 186:221-242.
 - [4] Ito H, Fukuda Y, Ozaki Y, Kondow T, Kuchitsu K. Analysis of perturbation between the $B^2\Sigma^+ v = 5$ and $A^2\Pi_J v = 17$ levels of the CN radical. J Molec Spectrosc 1987; 121:84-90.
 - [5] Engleman R. The $\Delta v = 0$ and $+1$ sequence bands of the CN violet system observed during the flash photolysis of BrCN. J Mol Spectrosc 1974; 49:106-116.
 - [6] National Solar Observatory (NSO) at Kitt Peak, McMath-Pierce Fourier Transform Spectrometer (FTS) data. [ftp://vso.nso.edu/FTS\\$_cdrom/FTS30/920212R0.005](ftp://vso.nso.edu/FTS/$_cdrom/FTS30/920212R0.005) (last accessed December 20, 2016).
 - [7] Parigger CG, Woods AC, Surmick DM, Gautam G, Witte MJ, Hornkohl JO. Computation of diatomic molecular spectra for selected transitions of aluminum monoxide, cyanide, diatomic carbon, and titanium monoxide. Spectrochim Acta Part B 2015; 107:132-138.
 - [8] Yurchenko SN, Lodi L, Tennyson J, Stolyarov AV. DUO: a general program for calculating spectra of diatomic molecules. Comput Phys Commun 2016; 202:262-275.
 - [9] Wigner E, Witmer EE. Über die Struktur der zweiatomigen Molekelspektren nach der Quantenmechanik. Z Phys 1928; 51:859-886. On the structure of the spectra of two-atomic molecules according to quantum mechanics. Hetttema H (Ed). Quantum Chemistry: Classic Scientific Papers. Singapore: World Scientific; 2000; 287-311.
 - [10] Zare RN, Schmeltekopf AL, Harrop DL, Albritton DL. A Direct Approach for the Reduction of Diatomic Spectra to Molecular Constants for the Construction of RKR Potentials. J. Mol. Spectrosc. 1973; 37-66.
 - [11] Brown JM, Howard BJ. An approach to the anomalous commutator relations of rotational angular momentum in molecules. Mol Phys 1976; 31:1517-1525.
 - [12] Lefebvre-Brion and Field R. W. The Spectra and Dynamics of Diatomic Molecules. Amsterdam: Elsevier; 2004.
 - [13] Brown JM, Carrington A. Rotational Spectroscopy of Diatomic Molecules. Cambridge: Cambridge Univ. Press; 2003, p. 516-517.
 - [14] Condon EU, Shortley GH. The Theory of Atomic Spectra. Cambridge: Cambridge Univ Press; 1964.
 - [15] Hilborn RC, Einstein coefficients, cross sections, f values, dipole moments, and all that. Am. J. Phys. 1982; 50:982-986.
 - [16] Thorne AP, Spectrophysics, 2nd. ed., New York: Chapman and Hall; 1988.
 - [17] Rothman LS, Rinsland CP, Goldman A, Massie ST, Edwards DP, Flaud JM, Perrin A, Camy-Peyret C, Dana V, Mandin JY, Schroeder J, McCann A, Gamache RR, Wattson RB, Yoshino K, Chance K, Jucks K, Brown LR, Nemtchinov V, Varanasi P. The HITRAN molecular spectroscopic database and HAWKS (HITRAN Atmospheric Workstation): 1996 Edition. J Quant Spectrosc Rad Transfer 1998; 60:665-710.
 - [18] Brown JM, Hougen JT, Huber KP, Johns JWC, Kopp I, Lefebvre-Brion H, Merer AJ, Ramsay DA, Rostas J, Zare RN. The labeling of parity doublet levels in linear molecules. J. Mol. Spectrosc. 1975; 55:500-503.
 - [19] Kovács I. Rotational Structure in the Spectra of Diatomic Molecules. American Elsevier, New York: American Elsevier; 1969.
 - [20] Li G, Harrison JJ, Ram RS, Western CM, Bernath PF. Einstein A coefficients and absolute line intensities for the $E^2\Pi - X^2\Sigma^+$ transition of CaH. J Quant Spectrosc Rad Transfer 2012; 113:67-74.